

21835

A Study of the Peroxides of Organic Acids.

A THESIS

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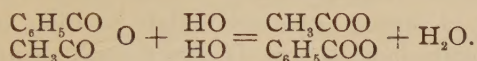
BY

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THE ACTION OF HYDROGEN PEROXIDE UPON ANHYDRIDES AND THE FORMATION OF ORGANIC ACID PEROXIDES AND PERACIDS.

Nef¹ has shown that pure hydrogen peroxide and acetic anhydride, reacting with each other, yield acetic peroxide. Baeyer² found that the same substance was formed by the action of acetic anhydride upon an aqueous solution of hydrogen peroxide. Neither of these authors attempt to explain the reaction which takes place, and one might be led to suppose that the peroxide was formed by the direct addition of oxygen to the anhydride. In considering the reaction of hydrogen peroxide upon benzoyl acetyl oxide Nef, however, assumes the following reaction to take place:



In attempting to prepare other peroxides by the action of anhydrides upon hydrogen peroxide it was found that only the anhydrides of the simple acids react with hydrogen peroxide, *i. e.*, anhydrides which are acted upon by water. Even when the more complex and less soluble anhydrides are brought together with hydrogen peroxide in ethereal solution there is no reaction.

From experimental facts, which will be brought out later, it will be seen that the action of hydrogen peroxide upon anhydrides is not a simple one: *That the reaction is very similar to that of water upon anhydrides, and the formation of peroxides depends upon two distinct reactions.*

Changes in Acetic Peroxide when Dissolved in an Aqueous Solution of Hydrogen Peroxide.

The changes which an aqueous solution of acetic peroxide undergoes have been previously considered. It was found that the substance was hydrolyzed with the formation of acetic acid and acetic peracid, and it was shown that acetic peracid could be distinguished from acetic peroxide by its very rapid action upon potassium iodide. The action of acetic peroxide in dilute solution upon potassium iodide, if the latter be not in large excess,

¹ Ann. Chem. (Liebig), **298**, 287.

² Ber. d. chem. Ges., **33**, 1569.

is so slow that the iodine liberated by the peracid may be estimated with little error.

It has been found that when acetic peroxide is dissolved in a solution of hydrogen peroxide there is a similar change into peracid, but that the amount of peracid in the solution is more than can be accounted for by the reaction of the peroxide upon water; moreover, that there is a gradual loss of hydrogen peroxide in the solution, the active oxygen of which is found combined with the acetyl group. In order to follow these changes it is necessary to be able to accurately estimate hydrogen peroxide, acetic peroxide and acetic peracid in the presence of each other.

In dilute solutions, containing no mineral acid, the action of hydrogen peroxide, as well as acetic peroxide, is so slow that, with practice, one may accurately estimate peracid by adding a drop or two of strong potassium iodide solution and titrating immediately with thiosulphate. If only a small amount of potassium iodide is added there need be no especial hurry in making the titration; after the removal of the "immediate" iodine, the further liberation can be seen to be very slow. If too much potassium iodide is used it is necessary to operate quickly and to make a preliminary titration to obtain approximately the amount of thiosulphate required; the estimation may then be made quickly. In either case, after a little practice, one may satisfy himself of the accuracy of the result.

The estimation of hydrogen peroxide may be accurately made by adding to a large excess of dilute sulphuric acid (2 N acid was used) and titrating with permanganate. It has been previously shown that peracids oxidize manganous salt to permanganic acid, and that this action interferes with the estimation as ordinarily made; however, in very dilute solution, which is strongly acidified, this action is so retarded that there is little error.

The following experiments illustrate the accuracy of the method:

10 cc. of a solution of commercial hydrogen peroxide titrated with N/20 permanganate, in the ordinary manner, required 23.7 cc. A strong solution of pure acetic peroxide¹ was made and allowed to stand four hours. At the end of this time the

¹ The acetic peroxide employed in this work was prepared according to the method previously described, and was recrystallized from ligroin just before using.

peracid in 1 cc. of the solution was represented by 6.1 cc. N/20 thiosulphate: the unchanged peroxide by 6.6 cc. Only a trace of hydrogen peroxide had been developed.

Separate portions of 10 cc. each of the above solution of hydrogen peroxide were then each diluted to 300 cc. with dilute sulphuric acid and cooled to 10°. To the first was then added 1 cc. of the above solution of acetic peroxide and peracid; to the second, 2 cc.; to the third, 3 cc.; and to the fourth, 4 cc. These solutions were then titrated with N/20 permanganate.

Required: 1, 23.65 cc.; 2, 23.60 cc.; 3, 23.65 cc.; 4, 23.55 cc.

In the fourth solution the amount of active oxygen as peracid was nearly equal to that as hydrogen peroxide. To obtain accurate results it is necessary to make the titration quickly, and to do this it is necessary, in case the amount of hydrogen peroxide in the solution is unknown, to make a preliminary titration in order to obtain approximately the volume of permanganate required.

The acetic peroxide cannot be directly estimated, but may be obtained by difference after estimating the total active oxygen. This may be accurately done by dissolving in a small amount of 20 per cent. acetic acid, containing potassium iodide and allowing to stand for a half hour, then diluting and titrating with thiosulphate. Careful experiments with known quantities of hydrogen peroxide, acetic peroxide and acetic peracid have shown that all of these substances may be accurately estimated in this way. A correction obtained from a blank solution may be applied.

A solution of commercial hydrogen peroxide containing 30.5 grams per liter was nearly saturated with pure acetic peroxide. The contents of the solution were estimated as quickly as possible after it was made and then at intervals. The temperature of the solution remained constant, 23°.

For the estimation of hydrogen peroxide 1 cc. of the solution was removed and diluted to 100 cc.; 50 cc. of this was removed and, after diluting to 300 cc. with dilute sulphuric acid, was titrated with N/20 permanganate, as already described. This number multiplied by two is the one given in the table.

For the estimation of peracid, 1 cc. of the solution was added

to 300 cc. of water, a small amount of potassium iodide solution added, and the iodine liberated, titrated quickly with N/20 thio-sulphate.

The total active oxygen contained in 1 cc. of the solution was determined by dissolving in 6 or 7 cc. of a 20 per cent. solution of acetic acid, containing potassium iodide and allowing to stand for one-half hour. The solution was then diluted and the free iodine estimated with N/20 thiosulphate. Only a slight correction, amounting to about 2 drops of thiosulphate is necessary.

The three portions to be estimated were removed from the original solution as quickly as possible after each other; after being diluted, as described, no further change takes place in the diluted solution during the time necessary to carry on the estimations.

Time in hours.	cc. N/20 thio- sulphate. (Immediate.)	cc. N/20 thio- sulphate. Total.	cc. N/20 per- manganate.	cc. N/20 thiosulphate representing acetic peroxide.
..		48.5	35.0	13.5
2	6.7	48.0	31.7	9.6
7	12.7	47.5	28.8	6.0
24	13.9	46.1	27.8	4.4

An inspection of these figures brings out the following facts:

(1) At the end of two hours the amount of active oxygen as peracid in the solution is just one-half of that originally present as peroxide. The formation of peracid is, therefore, much faster than in aqueous solution.

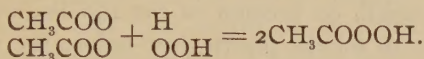
(2) Hydrogen peroxide gradually and rapidly separates from the solution: further the solution gradually loses in total active oxygen, but the loss in hydrogen peroxide is much greater than the loss in total active oxygen.

(3) At each interval the total active oxygen present as peroxide and peracid is considerably greater than that originally present as peroxide. Acetic peracid is therefore formed at the expense of the active oxygen of the hydrogen peroxide.

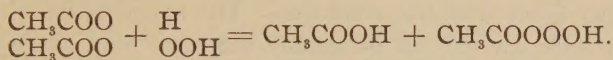
The solution of hydrogen peroxide employed contained a small amount of soluble mineral matter, which has a much greater catalytic action upon acetic peracid than upon hydrogen peroxide. This partly accounts for the loss in active oxygen; however, this loss was greatest during the first stages of the reaction at the time

when the amount of peracid was smallest. Active evolution of oxygen in the solution was most noticeable during the first hour or two. The greater part of the loss is, therefore, intimately connected with the reaction itself. During the last stages of the reaction the peracid is evidently decomposed faster than it is formed.

The action of hydrogen peroxide upon acetic peroxide resulting in the formation of more peracid than would be formed by the ordinary hydrolysis, is most easily explained as follows:



Owing to the instability of the substances in question it is not possible to say that they react in the proportion indicated. The reaction suggests that of water upon acetic peroxide. Looked on in this light the possibility of a reaction, according to the following equation, suggests itself:



Assuming such a reaction to take place, the loss of oxygen, already referred to, would be accounted for, by the instability of the substance CH_3COOOOH , a derivative of the hypothetical trioxide of hydrogen.

A number of experiments, similar to the one described, were carried out with different solutions of hydrogen peroxide, and in all cases similar results were obtained.

Action of an Aqueous Solution of Hydrogen Peroxide upon Acetic Anhydride.

When acetic anhydride is dissolved in hydrogen peroxide solution both acetic peracid and peroxide are soon present in the solution. The peracid in the solution may result from the hydrolysis of previously formed peroxide, or it may be formed directly by the action of hydrogen peroxide upon anhydride. A study of the rates of formation of these two substances has led to the conclusion that the peracid is the first substance formed.

The rate of formation of peracid in solution of hydrogen peroxide of different strength is shown in the table given below.

The best commercial hydrogen peroxide was used, which was concentrated to the strength given by distillation in vacuum. The acetic anhydride was fractionated before using.

Twenty cc. of hydrogen peroxide solution (61.6 grams per liter) were brought to a temperature of 21° and 1 cc. of acetic anhydride added. The latter was dissolved quickly by shaking and the solution was kept at 21° . At different intervals 1 cc. of the resulting solution was removed and the peracid present estimated in the manner already described. As the intervals of time are necessarily small, on account of the rapidity of the reaction, it was necessary to fill the pipette just before the time indicated and at the proper time to deliver the solution into a large volume of water, in order to stop or greatly retard any further reaction between the constituents. The results obtained appear in the first column below; in the second column are the results of a duplicate experiment carried out in exactly the same manner.

A solution of hydrogen peroxide of different strength (45.4 grams per liter) was also employed. The experiments with this solution were carried out in exactly the same way as described above, all conditions and measurements being the same. The results duplicated are placed in columns 3 and 4.

Time in minutes.	(1) N/20 thiosulphate.	(2) N/20 thiosulphate.	(3) N/20 thiosulphate.	(4) N/20 thiosulphate.
3	1.0	1.0	0.7	0.75
6	1.4	1.3	0.9	0.9
9	1.6	1.5	1.0	1.0
12	1.7	1.65	1.1	1.1
15	1.8	1.75	1.2	1.2
18	1.9	1.95	..	..
21	..	2.2	..	..
27	..	2.5	..	..
30	..	2.6	..	..

It will be noted that the rate of formation of peracid is large at first, but is soon checked. So long as acetic anhydride is present in the solution there would be a limit to the concentration of peracid owing to the ready reaction between the two substances, which has previously been pointed out. As soon as anhydride is removed from the solution the formation of peracid by the hydrolysis of peroxide should continue at a uniform rate. To

determine whether or not the relatively large amounts of peracid present in the solution, at the earlier intervals, can be accounted for by the hydrolysis of peroxide present, necessitates a determination of the amount of the latter substance in the solution at different intervals.

The amount of acetic peroxide was obtained as in the previous case, by subtracting from the total active oxygen the sum of the active oxygen as hydrogen peroxide and as peracid. The total active oxygen was obtained in the manner already described. The hydrogen peroxide was also estimated as previously described. Careful experiments showed that a known amount of hydrogen peroxide could be accurately estimated under the conditions employed and in the presence of the maximum amount of peracid, peroxide and anhydride, which might be in the solution to be examined. As this determination is of vital consequence to the results obtained and the conclusions drawn, a few of these experiments will be given.

A definite volume of hydrogen peroxide solution was estimated in the usual manner with N/20 permanganate. Required, 16.8 cc.; duplicated, 16.85 cc.

The same volume of hydrogen peroxide was added to 250 cc. of dilute sulphuric acid (2 N) and again estimated. Required, 16.85 cc.; duplicated, 16.85 cc.

The same volume of hydrogen peroxide was added to 250 cc. of dilute sulphuric acid (2 N). 0.05 gram of acetic anhydride was added, together with a solution of acetic peroxide, which had stood four or five hours and was equivalent to 4 cc. N/20 thiosulphate, "immediate," and 9 cc., total. Required, 16.85 cc. permanganate.

The estimation of acetic peroxide in this manner is dependent upon three other determinations, each of which is liable to a reasonable experimental error. The numbers obtained are, therefore, approximate ones, but are all that are to be desired.

The following experiments were made with the same solutions of hydrogen peroxide as were previously employed in the estimation of peracid, and were carried out in exactly the same manner, care being taken to make all conditions and measurements the same. The portion to be estimated for hydrogen peroxide was

delivered into 500 cc. of water at the proper time. Only a portion of this was titrated, the numbers appearing in the table representing the entire amount. It was not necessary to remove the portion to be estimated for total active oxygen at exactly the time indicated, as there is little variation in this value, during the time of the experiment. The figures in the table represent the amounts of N/20 solution required by 1 cc. of the reaction mixture.

HYDROGEN PEROXIDE, 61.6 GRAMS PER LITER.

Time in minutes.	Total thiosulphate.	Immediate thiosulphate.	Permanganate.	Thiosulphate representing peroxide.
3	68.7	1.0	66.95	0.75
6	68.8	1.35	66.1	1.35
18	68.7	1.9	64.4	2.4
30	68.9	2.6	64.2	2.1

HYDROGEN PEROXIDE, 45.4 GRAMS PER LITER.

Time in minutes.	Total thiosulphate.	Immediate thiosulphate.	Permanganate.	Thiosulphate representing peroxide.
3	51.0	0.7	49.9	0.4
6	50.8	0.9	48.1	1.8
18	50.8	1.3	46.65	2.85

Repetition of these experiments a number of times gave values which varied within a comparatively narrow range, for reasons already mentioned. In no case, however, were the numbers found to exceed those given by more than 1.0.

Experiments were made to determine the rate of hydrolysis of acetic peroxide in a solution of hydrogen peroxide. The solutions of hydrogen peroxide used were the same as in the previous experiments. A solution of acetic peroxide (approximately N/5) was made by dissolving 1.2 grams of pure acetic peroxide in 100 cc. of hydrogen peroxide. This concentration of acetic peroxide is considerably greater than that at any time in either of the solutions examined. The temperature remained at 21°. The peracid in 1 cc. of the solution was estimated at intervals in the usual manner. The amount is represented in the tables below N/20 thiosulphate, column 1 representing the stronger solution of hydrogen peroxide, and column 2 the weaker.

Time in minutes.	(1)	(2)
2	0.2	0.2
4	0.3	0.3
8	0.45	0.4
16	0.8	0.6

These numbers are to be compared with those obtained for peracid in the previous experiments. It is evidently impossible to account for the amount of peracid in those solutions, assuming that it is formed by the hydrolysis of acetic peroxide. The comparison applies especially to the earlier stages of the reaction. It is known that later acetic peroxide is formed in considerable amount, and that this eventually hydrolyzes to peracid.

To make sure that the acetic acid present in the original experiment had no accelerating action on the rate of hydrolysis of the peroxide, the reactions were compared in hydrogen peroxide solution of about 5.5 per cent., and in a 10 per cent. acetic acid solution, containing the same concentration of hydrogen peroxide. The same amount of pure acetic peroxide was added to each solution. The amounts of peracid formed at intervals in 1 cc. of the solutions, as represented by N/20 thiosulphate, are given below:

Time in minutes.	Acetic acid solution.	Unacidified solution.
20	0.3	1.1
40	0.6	1.8
60	0.8	2.3

It will be seen that the acid has a retarding, rather than an accelerating, influence.

It is evident that *acetic peracid results directly from the action of acetic anhydride upon hydrogen peroxide*, probably according to the following equation:



This reaction is analogous to that of acetic peroxide upon hydrogen peroxide, already considered. Here again we must notice the *similarity between the action of hydrogen peroxide and ordinary hydrolysis by means of water*.

It has been previously shown that peracids, even in very dilute solutions, are extremely reactive toward substances capable of

ordinary hydrolysis. It was shown that either benzoic or acetic peracids could be almost completely converted into benzoic acetic and acetic peroxides respectively, even in very dilute aqueous solution, by the addition of a small amount of acetic anhydride to the solution. The formation of the peroxide is, therefore, to be explained by the action of peracid upon unchanged anhydride. The great tendency for these substances to react is seen in the sudden check in the rate of formation of peracid during the reaction of acetic anhydride upon the solution of hydrogen peroxide.

Propionic anhydride was also found to show the same general behavior toward hydrogen peroxide as acetic anhydride. Its action is slower, but on account of its sparing solubility it is less suitable for study.

Since acetic peroxide is almost completely changed to peracid, in the course of twenty-four hours, experiments were made to determine the practicability of preparing a solution of acetic peracid by allowing a solution of anhydride in hydrogen peroxide to stand for this length of time.

(1) Two cc. of acetic anhydride were added to 100 cc. of a 3.2 per cent. commercial hydrogen peroxide solution, and kept cool by immersing in a vessel of water. After twenty-four hours the total amount of peracid in the solution, estimated in the usual manner, was 0.33 gram. From this it follows that about 22 per cent. of the anhydride entered into reaction with hydrogen peroxide.

(2) Five cc. of acetic anhydride were added to 100 cc. of the same hydrogen peroxide solution and kept cool. After twenty-four hours the solution contained 0.82 gram peracid. Here again 22 per cent. of the anhydride entered into combination with the hydrogen peroxide.

(3) Ten cc. of anhydride were added to 100 cc. of the same hydrogen peroxide solution and kept cool. After twenty-four hours there were 1.54 grams of peracid in the solution. In this case 21 per cent. of the anhydride entered into reaction with the hydrogen peroxide.

These experiments bring out an important fact; namely, that the rate of the reaction of hydrogen peroxide with anhydride is much greater than that of water with anhydride. From the rela-

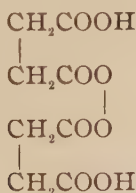
tive concentrations of the two substances in the above solutions it might be expected that if the rates were nearly equal, only a little over 3 per cent. of the anhydride would have reacted with the hydrogen peroxide. The fact that about the same per cent. was obtained in the three experiments shows that the acetic acid has little influence upon the relative rates. An excess of hydrogen peroxide was present in each experiment. In the third only a little over 20 per cent. of the hydrogen peroxide was used, and in the others much less. The secondary reaction of anhydride upon peracid would only tend to destroy the anhydride, and decrease the yield of peracid, as the active oxygen remains the same after this reaction.

A much better yield of peracid may be obtained by using a stronger solution of hydrogen peroxide, easily obtained by concentrating in vacuum.

Twenty cc. of a solution of hydrogen peroxide, containing 104 grams per liter, were added to 6.1 grams of anhydride, and the mixture shaken and kept cool until the anhydride had gone into solution. It was then allowed to stand in a vessel of water for twenty-four hours. At the end of this time hydrolysis was complete, and the solution contained about 2 grams of peracid, about 45 per cent. of the theoretical yield.

ANHYDRIDES OF DIBASIC ACIDS.

Succinic Peroxide Acid,



When a 3 per cent. solution of hydrogen peroxide is saturated with succinic anhydride, the oxidizing power of the solution rapidly changes, as can be noted by its effect on potassium iodide. The products of the reaction remain dissolved, however, as there is no precipitation from the solution. If a stronger solution of hydrogen peroxide be employed and excess of anhydride be

added, and the mixture shaken, so as to keep the solution saturated with the anhydride, a precipitation soon occurs. The anhydride used was in the form of broken pieces of a solid product, and after agitation, it quickly settled to the bottom of the vessel. The precipitate consists of very fine crystals, and remains suspended in the liquid. After a considerable quantity formed it was filtered, washed several times with water, dried quickly by packing tightly on a porous plate, then pulverized and allowed to remain in vacuum for several hours. For analysis, it was recrystallized from acetone. The active oxygen was estimated by dissolving the substance in a small amount of water, adding excess of potassium iodide, and titrating at once with standard thiosulphate.

0.2383 gram gave 0.0871 gram H_2O and 0.3563 gram CO_2 .

0.1232 gram required 20.82 cc. N/20 thiosulphate.

	Calculated for $C_8H_{10}O_8$.	Found.
H	4.31	4.10
C	41.0	40.78
Active O	6.84	6.78

The amount of succinic acid present in the substance, after complete hydrolysis and removal of active oxygen, was determined and found to agree with the theoretical.

The substance was covered with about twenty parts of water in a test-tube, a pinch of platinum-black added and allowed to stand for a week; the succinic acid formed was then estimated by titrating with N/10 potassium hydroxide.

0.1954 gram substance required 33.25 cc. N/10 KOH. Calculated, 33.40 cc.

0.1290 gram substance required 22.0 cc. N/10 KOH. Calculated, 22.05 cc.

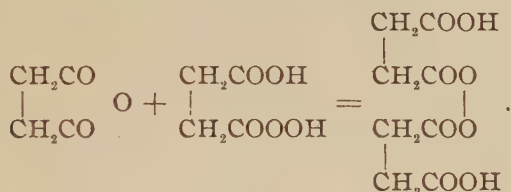
The substance is moderately soluble in water, alcohol, acetone and acetic ether; sparingly in ether; insoluble in chloroform, benzol and ligroin. It is colorless and, when pure, odorless. The crystals are flat plates, generally very irregular. The substance begins to soften at 115° and is completely melted at 128° , with decomposition. When brought into a flame it explodes; it does not explode on percussion or friction. When openly exposed to

the air it slowly deteriorates, but when well stoppered no deterioration could be detected after several months.

Assuming the action of succinic anhydride upon hydrogen peroxide to be similar to that of acetic anhydride, the first step is the formation of succinic monoperacid.



At the same time a certain amount of anhydride undergoes ordinary hydrolysis with water with the formation of succinic acid. The strength of the hydrogen peroxide solution employed determines the proportion in which the anhydride enters into each of these reactions. Succinic monoperacid is very soluble in water and does not separate from the solution. The second step in the formation of the peroxide acid is the action of succinic monoperacid upon succinic anhydride.



The best yield of the peroxide acid is obtained by employing a 7.5 to 8 per cent. solution of hydrogen peroxide.

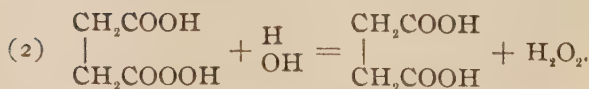
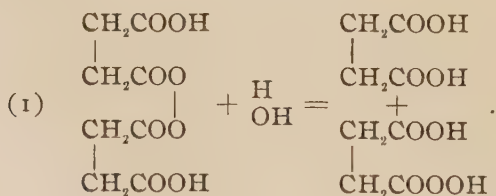
Ten grams of ordinary crystalline succinic anhydride were added to 25 cc. of 7.5 per cent. hydrogen peroxide and the mixture shaken. The temperature gradually rose, but was kept below 30°. At the end of thirty-five minutes there was no further rise in temperature, indicating that all anhydride had been dissolved. The product was then filtered and washed several times with small portions of water. It was then packed tightly on a porous plate, placed in a warm place, and after an hour, was perfectly dry. An analysis showed the substance to be pure, yield, 7.5 grams.

When excess of the peroxide is added to water and shaken the amount dissolved gradually increases. This increase is due to

the hydrolysis of the dissolved peroxide, which takes place according to the laws previously developed. The rate of the reaction is much greater than that with any peroxide previously studied.

An excess of finely pulverized peroxide was continuously shaken with water at about 24° . At intervals of five, ten, fifteen and twenty-five minutes a small portion of the mixture was filtered and the amount of peroxide dissolved was determined. At the end of five minutes the solution contained 19.8 grams per liter; at the end of ten minutes 24.5 grams per liter; at the end of fifteen minutes 28.4 grams per liter; and at the end of twenty-five minutes 35.8 grams per liter. At this rate of hydrolysis the original solubility may be placed approximately at 15 grams per liter. At the end of fifteen minutes the original solubility is almost doubled.

A large excess of peroxide was added to water in a beaker and kept stirred continuously for several hours. The rate of hydrolysis, as indicated by the active oxygen content of the solution, was found to decrease as the solution became stronger. At the end of one-half hour hydrogen peroxide could easily be detected in the solution by means of the titanous or chromic acid tests. After six hours an appreciable portion of the active oxygen of the solution (over 0.5 per cent.) was present as hydrogen peroxide. By this means it was possible to obtain a very strong solution of the hydrolysis products. The substance hydrolyzes according to the following equations. The second change is much slower than the first.



Succinic peroxide acid presents a striking difference from other

bodies of the peroxide type in the behavior of the unhydrolyzed substance toward potassium iodide. The action of the peroxide, as well as its hydrolytic product upon potassium iodide, is almost immediate, so that the substances cannot be distinguished from each other, as could the peroxides and peracids of monobasic acid. When excess of potassium iodide is added to a fresh saturated solution of the peroxide acid, or to the same solution after standing an hour, and which would, therefore, be mostly hydrolyzed, the calculated amount of iodine is liberated in the short time required to make the titration with standard thiosulphate. If the solution is very dilute, a minute or two is required before the liberation of iodine is complete. It was not possible, therefore, to study the hydrolysis of the peroxide acid in dilute solution. The change into hydrogen peroxide could be followed, however, by comparing the immediate liberation of iodine with the total.

The following figures indicate the gradual formation of hydrogen peroxide: (1) In a 1 to 1000 solution, and (2) in a 1 to 100 solution.

Time in days.	(1) Per cent. of active oxygen as H_2O_2 .	(2) Per cent. of active oxygen as H_2O_2 .
1	7.3	5.3
2	14.0	8.3
7	41.0	40.0

The active oxygen content of the weaker solution had not appreciably decreased at the end of one week. In the stronger solution there was a decrease of only 1.5 per cent.

In addition to its action on potassium iodide, the following are interesting properties, possessed by a solution of succinic peroxide acid. A small amount of manganous salt added to the solution soon produces the deep rose-red color of permanganic acid. The reaction is an extremely delicate test for traces of manganese. The coloration is prevented by the presence of considerable mineral acid. An excess of manganese salt gives, of course, manganese dioxide. The red solution of cobaltous salt is changed to an emerald-green, owing probably to the formation of a cobaltic salt; the solution slowly evolves oxygen. The addition of sodium acetate to the solution produces a precipitate, probably

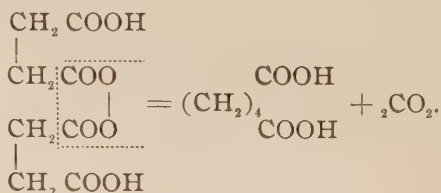
a higher oxide of cobalt. The green solution of a nickelous salt is soon changed to a purple, which is probably due to the formation of a nickelic salt. The latter seems to be unstable, however, as the solution evolves oxygen and, in the course of a few hours, the purple color disappears. The addition of sodium acetate to the purple solution causes an immediate change to green, with evolution of oxygen.

Finely divided manganese dioxide appears to have no catalytic action upon a solution of the peroxide acid, but is oxidized, in part, to permanganic acid. Lead dioxide has no catalytic action, but platinum-black has a slight action. The solution has no effect upon chromic acid, titanous acid, or potassium permanganate, until it has stood an hour or more, and hydrogen peroxide has been formed.

As already stated, succinic peroxide acid, like all peroxides, decomposes when heated. The decomposition was studied by adding the substance to xylol, which was heated to its boiling-point. Carbon dioxide was evolved, the amount being a little less than 1 molecule per molecule of peroxide. Only a trace, if any, of oxygen or hydrocarbons was evolved. On cooling the xylol a crystalline product separated, which was about 50 per cent. of the original weight of substance. This product consisted chiefly of succinic anhydride, which was removed by digesting with chloroform on the water-bath. The residue was distilled, whereupon water, succinic acid and anhydride passed over. The residue from this distillation consisted chiefly of adipic acid, which was recrystallized from water and identified by its melting-point.

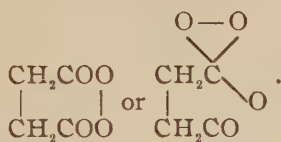
0.1204 gram required 16.45 cc. N/10 KOH. Calculated for adipic acid, 16.45 cc.

From the original xylol solution there was obtained, after removal of the solvent, a gummy residue, which dissolved completely in sodium carbonate. It was not identified. A small portion of the substance, therefore, decomposes as follows:



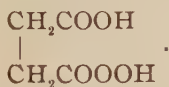
The major portion, however, decomposes to yield succinic anhydride, and the gummy acid substance already mentioned.

Vanino and Thiele¹ have described a substance obtained by the action of succinyl chloride upon sodium peroxide hydrate, which they have called succinyl peroxide and to which they have assigned the formula $C_4H_4O_4$. Baeyer and Villiger² have pointed out that the insolubility of the substance in water and in all other solvents renders improbable such a simple formula as the one assigned. The substance was prepared according to the directions of Vanino and Thiele in order to determine the per cent. of active oxygen. There is no way to purify the substance so that the crude product, well washed and dried, was used. This product may be an individual substance or it may be a mixture. The yield obtained was very small. If the substance is covered with a 20 per cent. solution of acetic acid and potassium iodide it gradually goes into solution after six or eight hours with the liberation of iodine. The per cent. of active oxygen, so estimated, was 10.5, a correction having been made for a blank. The per cent. calculated for $C_4H_4O_4$ is 13.8. The substance is described in Richter's "Chemie der Kohlenstoff-Verbindungen" as having either the formula



There is certainly no ground at present for assigning any formula to the substance, even assuming that the product in question is homogeneous in composition.

Succinic Monoperacid,



Ten grams of succinic peroxide acid were covered with about 75 cc. water in a beaker and stirred continuously at a tempera-

¹ Ber. d. chem. Ges., 29, 1724.

² *Ibid.*, 34, 762.

ture of about 30° . At the end of three or four hours the entire amount had gone into solution. It was then removed to an evaporating dish and allowed to remain in vacuum over night with sulphuric acid. The dry residue consisted of about 45 per cent. of succinic monoperacid. The monoperacid is more soluble in chloroform than succinic acid, and may be removed from the latter by digesting the mixture with chloroform at 50° , filtering and cooling the solution. In this way the substance is obtained fairly pure. It may be recrystallized from a mixture of chloroform and ether, from which it separates in large crystals on standing. The per cent. of active oxygen, contained by various samples, which were recrystallized several times, varied from 10.5 to 11.3, while the theoretical is 11.9. This deficiency may have been due to the fact that when the substance is dissolved in water a decided evolution of oxygen is noticeable; it was necessary to dissolve in water to estimate the active oxygen. A sample recrystallized twice contained 11.0 per cent. of active oxygen and, when rapidly heated, melted at 107° with decomposition.

0.1170 gram gave 0.0473 gram H_2O and 0.1546 gram CO_2 .

	Calculated for $C_4H_6O_5$.	Found.
C	35.81	36.03
H	4.52	4.53

The substance is much more soluble in water than succinic acid; the same relation exists between the solubilities of benzoic acid and peracid. It also dissolves freely in alcohol, acetone and acetic ether. It is only moderately soluble in ether and sparingly in chloroform. It has very little, if any, odor, and does not, in the least, remind one of hypochlorous acid, as do benzoic and acetic peracids. It gradually decomposes on standing, but is more stable than benzoic peracid. A sample, consisting of a mixture of succinic acid and monoperacid, was found, on analysis, to consist of 60 per cent. of the latter. After standing for a week in a stoppered vessel the per cent. of monoperacid was only 55.4.

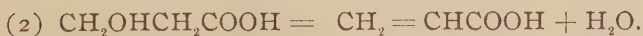
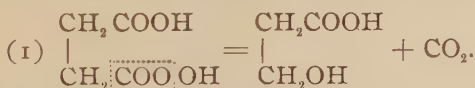
When a strong aqueous solution of the substance (either pure or mixed with succinic acid) is saturated with succinic anhydride, a heavy precipitate of succinic peroxide acid soon appears; more quickly on cooling and scratching with a glass rod. When

glutaric anhydride is dissolved in a strong solution of the monoperacid the mixed peroxide acid of succinic and glutaric acids is formed and, on cooling, separates from the solution. This substance will be described later.

The decomposition of succinic monoperacid is interesting. The mixture of acid and monoperacid was used for this study. It was mixed with infusorial earth in order to moderate the action.

3.5 grams of the mixed acids, containing 1.6 grams of monoperacid, were mixed with 5 grams of infusorial earth and placed in a small flask connected with the carbon dioxide generator and a gasometer. The air in the flask was completely replaced by carbon dioxide and the flask was then slowly heated in an oil-bath, and the gas evolved was collected over water in the gasometer. The volume of gas evolved was about 350 cc. This consisted almost entirely of carbon dioxide, with only a trace of oxygen and a small amount (about 3 per cent.) of a combustible gas. The amount of carbon dioxide obtained is a little in excess of 1 molecule from one molecule of the monoperacid.

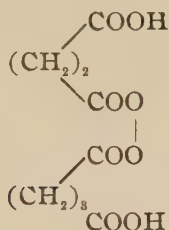
The experiment was repeated in order to determine the nature of the non-gaseous products. After the decomposition was completed the contents of the flask were distilled. Considerable water passed over at first and the temperature gradually rose to 140°. The distillate possessed the characteristic odor of acrylic acid. That it consisted, in a large part, of this substance was shown by treating it with concentrated hydriodic acid, whereupon β -iodopropionic acid crystallized from the solution. This was recrystallized from water and identified by its melting-point. The decomposition may be explained as follows:



The substance first splits off carbon dioxide. The β -hydroxypropionic acid, which is probably formed as an intermediary product, then splits off water with the formation of acrylic acid. The decomposition probably takes place almost entirely in the manner indicated. Baeyer found that benzoic peracid decom-

posed with the formation of benzoic acid and oxygen. The results obtained with succinic monoperacid have suggested that possibly phenol is also formed during the decomposition of benzoic peracid. This is made probably from the fact that benzoic peracid becomes colored on standing. Phthalic monoperacid, discovered and described by Baeyer, was found to yield salicylic acid on decomposition; this was identified by its color-test with ferric chloride.

Succinic Glutaric Peroxide Acid,



Ten cc. of a solution of succinic monoperacid, containing 1.47 grams of this substance and which was free from hydrogen peroxide, were treated with 1.5 grams of glutaric anhydride. The latter substance was dissolved after shaking for a minute. The solution was kept cool under a tap and after about five minutes a crystalline precipitate appeared. After standing for five minutes longer the product was filtered, washed several times with small portions of water and packed tightly on a porous plate. When dry, the substance was practically pure. Yield, 1.2 grams. For analysis, it was recrystallized from a mixture of ether and acetic ether.

0.0825 gram required 13.25 cc. N/20 thiosulphate.

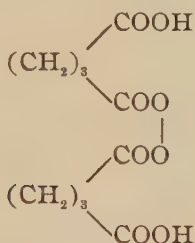
0.14.73 gram gave 0.0650 gram H_2O and 0.2344 gram CO_2 .

	Calculated for $\text{C}_9\text{H}_{12}\text{O}_8$.	Found.
C	43.52	43.40
H	4.88	4.96
Active O	6.45	6.40

The substance begins to soften at 105° and melts at 107° with

decomposition. It is quite soluble in alcohol, acetone and acetic ether, and sparingly soluble in ether. The crystals are similar in appearance to those of succinic peroxide acid. When potassium iodide is added to a saturated solution of the substance, it must stand two or three minutes before the theoretical amount of iodine is liberated. In oxidizing action it is, therefore, less powerful than succinic peroxide acid.

Glutaric Peroxide Acid,



Three grams of glutaric anhydride were dissolved in 6 cc. of 8 per cent. hydrogen peroxide. The solution was kept cool and the peroxide acid soon crystallized out. After twelve minutes it was filtered off, washed well with small portions of water and dried on a porous plate. The dried substance was practically pure. Yield, 1.9 grams. For analysis, it was crystallized from acetic ether.

0.0888 gram required 13.25 cc. N/20 thiosulphate.

0.1578 gram gave 0.0756 gram H_2O and 0.2640 gram CO_2 .

	Calculated for $\text{C}_{10}\text{H}_{14}\text{O}_8$.	Found.
H	45.77	45.61
C	5.39	5.37
Active O	6.10	5.97

The substance melts sharply at 108° with decomposition. It is quite soluble in alcohol, acetone and acetic ether; moderately soluble in ether; and very sparingly in chloroform and benzol. The substance hydrolyzes in aqueous solution, and the solubility and rate of hydrolysis were determined at 24° , in the same manner as with succinic peroxide acid.

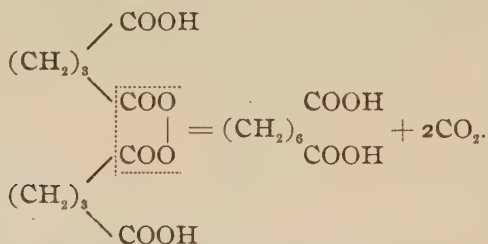
The amounts of peroxide acid, contained in 1 liter of solution at intervals of five, ten, fifteen and twenty-five minutes, were 9.75, 10.75, 11.6 and 13.75 grams respectively. At this rate of hydrolysis the original solubility may be placed approximately at 8.75 grams per liter.

The action of glutaric peroxide acid upon potassium iodide is markedly different from that of succinic peroxide acid. The action is very slow, like that of hydrogen peroxide. As in the case of the latter substance, the time required for the complete liberation of iodine is greatly decreased by the addition of dilute sulphuric acid. Except in very dilute solution of peroxide the theoretical amount of iodine is liberated in fifteen minutes when excess of potassium iodide has been added.

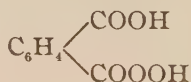
The decomposition of glutaric peroxide acid was studied in the same manner as that of succinic compound.

4.5 grams of the substance were added in small portions to 15 cc. of boiling xylol. The non-volatile products of decomposition remained dissolved, but on cooling, 0.6 gram of colorless crystals was deposited. This product was found to be almost pure, suberic acid. The substance was purified by recrystallizing from water and melted at 140° (suberic acid 140°).

0.1156 gram required 13.45 N/10 KOH. Calculated, 13.3 cc. On distilling off the xylol from the filtrate, previously mentioned, a fatty residue remained, which was soluble in sodium carbonate. The decomposition takes place only to a certain extent as follows:

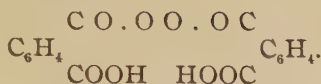


By the action of sodium hydroxide and hydrogen peroxide upon phthalic anhydride, Baeyer and Villiger¹ have isolated phthalic monoperacid,

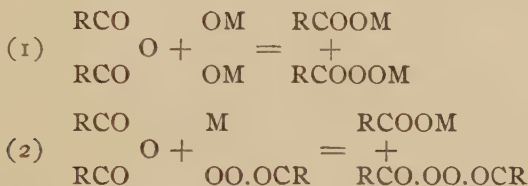


¹ Ber. d. chem. Ges., 34, 762.

and phthalic peroxide acid,



These authors have offered no explanation of the reactions involved. If we consider that the addition of an alkali to a solution of hydrogen peroxide results in the formation of a salt of this substance, either MOOH or MOOM, then the reaction between such a solution and an anhydride may be looked upon as follows:



Such a view would explain all of the reactions which are known to take place between sodium peroxide, barium peroxide, etc., and acid anhydrides, chlorides, etc. This explanation is, however, not in accord with the views of Calvert,¹ who, after attacking from all sides the problem of the condition of hydrogen peroxide in alkaline solution, arrived at the conclusion that a compound of the type MO_2 is formed, M being a monovalent metal. The work of Calvert has certainly shown that 1 molecule of alkali is capable of holding in combination more than 1 molecule of hydrogen peroxide. This behavior might be due to the formation of an addition compound between hydrogen peroxide and its primary salt, such as KHO_2 , H_2O_2 . Schöne² has isolated compounds of this type by evaporating an alkaline solution of hydrogen peroxide in vacuum. A compound³ containing sodium acetate and hydrogen peroxide crystallizes out on adding sodium peroxide to acetic acid. Tanatar⁴ has isolated compounds between other salts and hydrogen peroxide. Calvert showed that the solubility of potassium chlorate is greater in a solution of hydrogen

¹ Ztschr. phys. Chem., **38**, 513.

² Ann. Chem. (Liebig), **193**, 241.

³ Tafel: Ber. d. chem. Ges., **27**, 816.

⁴ Ztschr. anorg. Chem., **28**, 255.

peroxide than in water, and that its electric conductivity is less, although it would be expected to be greater, on account of the dielectric constant of hydrogen peroxide being greater than that of water. Jones and Carroll¹ further found that the depression of the freezing-point, brought about by various salts in hydrogen peroxide solution, is less than that in water, and have pointed out the probability that compounds are formed between hydrogen peroxide and salts in solution. An unstable compound between the benzoylated hydrogen peroxide and its sodium salt has been observed by Baeyer and Villiger.² A number of weak acids are known to form compounds of this type, and we may even look at compounds containing water of crystallization in the same light. It is not known whether or not such compounds are completely dissociated in aqueous solution. The similarity between hydrogen peroxide and water, which has been pointed out in this article, makes it appear possible that water enters into combination with neutral salts dissolved in it. In this connection, the results obtained by Calvert and by Jones and Carroll appear especially interesting.

The following may be summed up as the chief reactions which are known to take place when an anhydride is dissolved in an aqueous solution of hydrogen peroxide:

- (1) Ordinary hydrolysis with water.
- (2) Analogous reaction with hydrogen peroxide resulting in the formation of a peracid.
- (3) Action of peracid on anhydride with the formation of an acid peroxide.
- (4) Ordinary hydrolysis of peroxide with water.
- (5) Action of hydrogen peroxide upon acid peroxide with the formation of two molecules of peracid and also with loss of oxygen, possibly due to the intermediary formation of a derivative of hydrogen trioxide.
- (6) Slow hydrolysis of peracid to acid and hydrogen peroxide.
- (7) Slow decomposition of both peracid and hydrogen peroxide with evolution of oxygen.

The author wishes to acknowledge his indebtedness to Dr. Paul C. Freer, at whose suggestion this field of work was undertaken,

¹ Am. Chem. J., **28**, 284.

² Ber. d. chem. Ges., **33**, 1569.

and to whose help and inspiration, during his student career, the author feels is largely due whatever he may have accomplished.

He also wishes to thank Mr. G. F. Richmond and Mr. A. C. Houghton for valuable help rendered during the course of these researches.

ANN ARBOR, MICH.,

February 13, 1904.

THE HYDROLYSIS OF ORGANIC ACID PEROXIDES AND PERACIDS.

In cases of autoxidation, hydroperoxide has been frequently met with. Kingzett¹ and Löw² have shown that in the case of oxidized turpentine oil the active oxygen is not originally present in the form of hydroperoxide, and Engler and Weissburg³ have further pointed out the fact that in all cases where hydroperoxide has been observed among the products of autoxidation its presence could be explained by assuming a secondary reaction of water with the original product. They look upon this change not as a direct oxidation process but as a hydrolytic one, *i. e.*, one brought about by the interaction of the substance in question with hydrogen and hydroxyl ions. They call attention to the fact that if benzoic peroxide be added to a solution of titanous acid in sulphuric acid, the latter, in time, takes on the yellow color produced by hydroperoxide, and they find that acetic peroxide gives this coloration almost immediately. They attribute these colorations to the formation of hydroperoxide.

Brodie,⁴ however, makes the statement that with water the peroxides separate into free acid and oxygen.

Baeyer⁵ has saponified benzoic peroxide with sodium ethylate, and acetic peroxide with sodium hydroxide. In the former case he isolated benzoperacid, and in the latter showed that the resulting product had acquired the properties of a peracid. He also points out that benzoic and acetic benzoic peroxides are sub-

¹ J. Chem. Soc. (London), **12**, 511; **13**, 210.

² Chem. Centrbl, 1870, p. 821.

³ Ber. d. chem. Ges., **31**, 3047.

⁴ Ann. Chem. (Liebig), Suppl., **3**, 211.

⁵ Ber. d. chem. Ges., **33**, 1569.

stances without action upon solutions of potassium iodide or indigo, and without odor, and concludes that the acquisition of such properties by these substances is probably to be attributed to a hydrolytic change in which peracids are formed.

Wolffenstein¹ has found that the peroxides of acetone and mesityl oxide separate hydroperoxide on warming with dilute sulphuric acid, and Baeyer² has further observed that phthalmonoperacid gives rise to hydroperoxide on heating the solution.

Numerous authors have noted the formation of hydroperoxide by the action of alkalis upon peroxides.

Freer and Novy³ have studied the action of water upon benzoic acetic peroxide, and have found that the active oxygen gradually goes into solution, while considerable quantities of benzoic peroxide are formed.

The most interesting and extensively investigated organic peroxides are those of the acids. These substances are to be considered as derivatives of hydroperoxide, and those which have been thoroughly investigated are found to belong to one of two classes:

(1) Peroxides, in which both of the hydrogen atoms in a molecule of hydroperoxide are replaced by acid radicals.

(2) Peracids, in which only one of the hydrogen atoms is so replaced.

With the object of discovering the exact nature of the changes which these bodies undergo with water, and of giving a general expression to the results obtained, several representative peroxides and peracids have been investigated. The work has led to the following conclusions:

(1) Acid peroxides are completely hydrolyzed by water into acid and peracid. The time taken to complete the change varies of course, with the nature of the peroxide and with its solubility in water. A 5 per cent. solution of acetic peroxide is completely changed in the course of forty-eight hours, while with butyric or crotonic peroxides the change is very much slower. With benzoic peroxide it is so slow as to be scarcely detected in the course of several days. This change is a complete one in all cases

¹ Ber. d. chem. Ges., 28, 2265.

² *Ibid.*, 34, 762.

³ This JOURNAL, 27, 161.

investigated, that is, the reaction is not reversible:



In case the peroxide is not homogeneous the hydrolysis may take place in two ways:



or



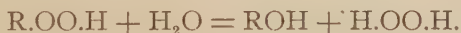
In the case of benzoic acetic peroxide the change was found to take place almost, if not altogether, completely in one way.

In the hydrolysis of peroxides of this class other products are met with, owing to a secondary reaction of the peracid first formed with the original peroxide. It has been found that peracids in aqueous solution are extremely reactive toward substances capable of hydrolysis, such as acid chlorides, anhydrides, and peroxides:



In all cases a peroxide is formed, together with an acid or a peracid. In case this peroxide is formed faster than it is hydrolyzed, it is evident that it will accumulate. In this way the less soluble and more slowly hydrolyzed homogeneous peroxide will be formed as a product of hydrolysis of a mixed peroxide, and the peracid which results from the reaction will be found in the solution.

(2) Peracids are hydrolyzed into acid and hydroperoxide:



The change is a much slower one than the corresponding peroxide hydrolysis and, following the general rule of hydrolytic processes, takes place much more rapidly in acid solution. This change is also a non-reversible one.

Acetic Peroxide.

Preparation.—Brodie¹ first prepared this substance by the

¹ *Loc. cit.*

action of barium peroxide upon acetic anhydride, the former being gradually added to a cooled ethereal solution of the latter. The yield which he obtained was very poor. Nef¹ prepared it by the action of pure hydroperoxide upon acetic anhydride, and Baeyer² makes the observation that it is formed by adding acetic anhydride to an aqueous solution of hydroperoxide. In working with considerable quantities of this substance, the method of Nef was found to be too laborious and that of Baeyer unsatisfactory as to yield. The action of barium dioxide upon acetic anhydride has again been studied and it has been found that, under proper conditions, nearly a theoretical yield of the acetic peroxide may be obtained. Twenty-two and a half grams of comparatively good barium dioxide (94 per cent.) were covered with 30 cc. of water and shaken for a few minutes with cooling. Twenty grams of acetic anhydride were added to 100 cc. of ether and cooled to 0°. The suspension of barium dioxide was then gradually added, with shaking, during the course of five minutes. The mixture was kept cooled to 0° and shaken for about fifteen minutes, when the dioxide had about disappeared. The ethereal layer was then removed by decantation, dried for several hours over calcium chloride, and the solvent then removed in a vacuum. The peroxide begins to crystallize from the cold, concentrated solution, and finally remains as a pure crystalline residue. It may be recrystallized from ligroin by cooling, in a freezing-mixture, a solution saturated at room temperature. Owing to the danger of spattering during the removal of the last portion of ether, it is advisable, on account of the extreme explosiveness of the substance, to dissolve the concentrated ethereal solution in ligroin and allow the peroxide to crystallize in a freezing-mixture. The yield was 8.8 grams. As the peroxide is probably formed according to the equation



this amount represents 76 per cent. of the total possible yield. Almost as good a yield may be obtained by using the cheaper and less pure barium dioxide, although in this case it is better to use more than the calculated amount, owing to the slow solu-

¹ Ann. Chem. (Liebig), **298**, 287.

² Ber. d. chem. Ges., **33**, 1569.

bility of portions of the commercial article. If the solution be kept well cooled the yield is not greatly decreased by using excess of the dioxide. The pure peroxide liberates the theoretical amount of iodine from a solution of potassium iodide (best in 20 per cent. acetic acid).

If the peroxide is dissolved in excess of N/10 potassium hydroxide and the solution heated on a water-bath for ten minutes, on titrating the excess of hydroxide the amount used will be found to correspond to 2 molecules for every molecule of peroxide.

The pure peroxide, shaken with water at 25° for five minutes, yielded a 0.935 normal solution of active oxygen. When the shaking was continued for ten minutes a 0.950 normal solution was obtained. At this rate of hydrolysis the real solubility may be placed at 0.920 normal, or 54.2 grams per liter.

As previously stated, this substance, like all acid peroxides having an appreciable solubility in water, liberates iodine from a solution of potassium iodide. The action of these substances in neutral or slightly acidulated solution is very slow, but is greatly increased in rapidity in more strongly acid solution. In this case, however, it is necessary to make a correction for the amount of iodine liberated from a blank solution under the same conditions. It is generally best to use acetic acid to acidulate with, as the solubility of the peroxides is thereby greatly increased.

If potassium iodide is added to a slightly acidulated, freshly prepared solution of acetic peroxide, there is no immediate liberation of iodine. On standing, however, the latter appears in the solution in gradually increasing concentration and the reaction is complete in three or four hours. If, however, the solution of peroxide is allowed to stand twenty-four hours before the addition of potassium iodide, its behavior is markedly different. In this case the liberation of nearly the entire amount of iodine takes place immediately. As will be shown later, the change which has produced this difference in behavior requires at least twenty-four hours to complete itself. As already noted, however, the liberation of iodine is complete in three or four hours in a non-hydrolyzed solution. This indicates that either a condition of equilibrium exists between the factors of the reaction, per-

mitting the reaction to go to completion much more quickly by the removal of one of the products, or that the unchanged peroxide is itself an oxidizing agent. However, from a saturated solution of acetic peroxide which had stood a week, it was impossible to extract any of the unchanged substance by means of ligroin. The peroxide is more soluble in ligroin than in water. A small amount of active oxygen is taken up by the ligroin, but the former oxidizes potassium iodide immediately, and is therefore due to acetperacid. As the presence of small quantities of unchanged peroxide would be indicated by a further slow liberation of iodine, it may be concluded that the change is a complete one. From this and the similar behavior of other peroxides, it is to be assumed that they are themselves oxidizing agents.

This gradual change which a solution of peroxide undergoes may be followed in a rough way by noting, from time to time, the amount of iodine liberated immediately, the iodine being estimated by means of a N/10 solution of sodium thiosulphate. Of a freshly prepared solution, 5 cc. required a total of 20.2 cc. N/10 thiosulphate; after four hours the immediate liberation of iodine required an average of 9.7 cc.; at the end of eight hours, 14.6 cc.; after twenty-two hours, 19.3 cc. The solution stood at a temperature of 20°. The titration was performed as quickly as possible after adding the potassium iodide, but even then the values obtained are not to be considered absolute, owing to the oxidizing action of the unchanged peroxide. The numbers indicate the general course of the change, however. A similar experiment with the analogously constituted propionic peroxide shows the progress of the change much more exactly.

Cryoscopic Data.—0.655 gram acetic peroxide was dissolved in 25.703 grams water in an ordinary Beckmann apparatus. A lowering of 0°.444 was produced.

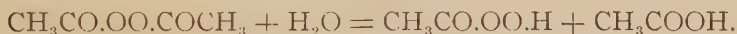
Molecular Weight.

Calculated.	Found.
118	109

The solution was then allowed to stand at 20° and additional readings of the freezing-point were taken from time to time:

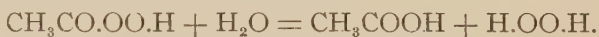
After	8 hours,	additional	lowering	0°.223
"	20	"	"	0°.338
"	24	"	"	0°.343
"	32	"	"	0°.363
"	44	"	"	0°.380
"	50	"	"	0°.377

Some little time was spent in dissolving the substance and getting conditions for the first reading, so that the latter is a little large, accounting for the low molecular weight found. At the end of two days there was little change in the freezing-point on further standing. The total depression of the freezing-point is 0°.821. The calculated depression caused by a hydrolysis of 1 molecule of peroxide into 2 molecules is 0°.820. It might not be expected that these numbers should agree quite so well, as it will be seen later that further changes take place in the solution. The experiment is in good agreement with the one in which the immediate liberation of iodine was estimated from time to time, and clearly demonstrates that the primary change is one in which 2 molecules are produced from one of the peroxide. As it will be shown further on that one of these substances is acetperacid, the change may be expressed as follows:



The Formation of Hydroperoxide.—If a saturated solution of acetic peroxide be subjected to the tests for hydroperoxide, only negative results are obtained, *i. e.*, chromic acid is not oxidized to perchromic acid, and a solution of titanous acid in dilute sulphuric acid is not colored. The latter solution, however, soon becomes yellow on standing, the more quickly, the more sulphuric acid is present, other conditions being the same. The rapid formation of hydroperoxide in this case is to be attributed to the hydrolytic influence of the sulphuric acid. In numerous cases in the literature, peroxides are described as responding to this test. It is highly probable that all such cases are due to the hydrolytic development of hydroperoxide due to the use of too strong sulphuric acid in preparing the titanous solution. None of the peroxides which were examined responded to this test except on standing. On the other hand, the delicacy of the perchromic acid test for hydroperoxide is greatly decreased by the use of mineral acid,

and for this reason it is more reliable, although not so delicate. It is easy to detect 1 part of hydroperoxide in 100,000 parts of water by covering the solution with ether, cooling, adding a grain of potassium bichromate, and then very dilute sulphuric acid drop by drop until the maximum coloration is produced. After the solution of acetic peroxide has stood for two hours, there are evidences of the formation of hydroperoxide by a slight immediate coloration with titanous acid. At the end of three hours a decided test is obtained with chromic acid. The first change, *i. e.*, the hydrolysis of acetic peroxide, has been shown to be practically complete in about two days. At the end of this time 93 per cent. of the active oxygen in the solution causes immediate liberation of iodine. As it has already been shown that the solution at this point contains practically no acetic peroxide, this remaining active oxygen is to be attributed to hydroperoxide, which, like the acetic peroxide, liberates iodine very slowly in dilute acetic acid solution. The amount of hydroperoxide continues to increase on standing, until at the end of a month nearly the entire active oxygen content of the solution is present in this form. It is evident, then, that the hydroperoxide results from the hydrolysis of the acetperacid,



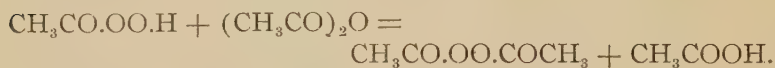
The following table shows the stability of a solution of acetperacid and the rate at which it is hydrolyzed into hydroperoxide. The numbers in the first column indicate the immediate liberation of iodine by 5 cc. of the solution, estimated as quickly as possible by a solution of N/10 thiosulphate; they represent acetperacid. The numbers in the second column indicate the total active oxygen in 5 cc. of the solution, due to acetperacid and hydroperoxide. In the third column are placed the differences between the total and immediate iodine representing hydroperoxide. Experiments with benzoperacid and hydroperoxide showed that, in dilute acetic acid, the two substances may be estimated in the presence of each other by this method:

Time in days.	Cc thiosulphate. Immediate.	Cc. thiosulphate. Total.	Difference.
0	0.0	40.2	
2	37.3	40.0	2.7
3	35.1	39.3	4.2
4	32.0	37.5	5.5
5	29.0	36.7	7.7
9	24.7	35.5	10.8
15	18.2	34.3	16.1
22	11.8	31.4	19.6
30	5.4	28.0	22.6
34	3.4	26.5	23.1

Further Evidence of the Presence of Acetperacid.—From the behavior of the hydrolyzed solution toward potassium iodide, and by comparison with the similar behavior of the benzoperacid of Baeyer, it has been assumed that acetperacid was one of the products of hydrolysis. The following experiments conclusively decide this point:

Action of Acetic Anhydride.—An aqueous solution of acetic peroxide was allowed to stand twenty-four hours. It was then extracted several times with ligroin, by which means small quantities of unchanged peroxide were removed, the hydrolyzed product being much more soluble in water and less soluble in ligroin than the peroxide. Two cc. of the solution then liberated iodine, requiring 14.2 cc. N/10 thiosulphate immediately and 0.8 cc. additional, due to hydroperoxide and unchanged acetic peroxide. Fifty-one cc. of this solution, representing 2.1 grams of acetic peroxide originally, were placed in a flask, cooled to 15°, and 4 grams of acetic anhydride added and dissolved by shaking. The solution was kept cooled to 15°. One cc. was removed at intervals (5 cc. in all), and the "immediate" titer was found to gradually decrease from its original value of 6.4 to 1.2 in about one-half hour, the total active oxygen content of the solution remaining the same (decreased slightly by the dilution with acetic anhydride). After this time it began to slowly increase again. After two hours it was extracted several times with ligroin. On evaporating the solvent and cooling, acetic peroxide crystallized out. 0.0764 gram analyzed for active oxygen required 12.7 cc. N/10 thiosulphate; calculated, 12.9 cc. The amount of peroxide removed by extracting four times with 0.5 volume of ligroin was 0.7 gram, and an additional amount remained in the solution.

It will be recalled that before the addition of acetic anhydride the solution had been thoroughly extracted with ligroin, and only a very small amount of peroxide was obtained. Further, that the amount of hydroperoxide in the solution would account for the formation of only a trace of acetic peroxide. The following reaction, therefore, took place:



Action of Benzoyl Chloride.—Twenty cc. of an aqueous solution of acetic peroxide (1 cc. required 6 cc. N/10 thiosulphate) stood twenty-four hours. To the solution were added 2 grams of benzoyl chloride and an excess of sodium acetate. The mixture was shaken in a flask at 25° for ten hours, in which time the product had solidified. The solid product was dissolved in ether and shaken out with a solution of sodium carbonate. On evaporation of the ether a crystalline residue remained which still retained the odor of benzoyl chloride, and was allowed to lie exposed to the air until this had disappeared. The residue consisted of a mixture of benzoic and benzoic acetic peroxides, the difference in their solubility in ligroin permitting of a separation. The latter substance separated from the mother-liquor with difficulty, owing to the presence of an oily impurity. After crystallizing several times, the melting-point could not be raised beyond 36° (Baeyer, 38° to 39°). At this point there was not enough of the substance left for analysis, but there is little doubt as to its identity. The original residue consisted of about 25 per cent. of the benzoic acetic peroxide, estimated in dilute acetic acid with potassium iodide and thiosulphate. The benzoic peroxide does not liberate iodine in dilute acetic acid. The benzoic acetic peroxide was probably formed according to the following equation:



The formation of benzoic peroxide here, in such large quantities, is noteworthy and interesting.

Acetperacid.—The isolation of this substance from an aqueous solution containing acetic acid presents great difficulties. As

the chief interest in this substance lies in its oxidizing properties, and as the solution as formed is quite well adapted for its use in this respect, there is no special need for its isolation. A few of the striking characteristics of the solution are as follows: Indigo is bleached slowly, more rapidly with the addition of dilute sulphuric acid. A weak solution of litmus is not decolorized by a large excess of the oxidizing agent in twelve hours. Chlorine is liberated from a dilute solution of hydrochloric acid. A drop of potassium permanganate is unaffected in a large excess of the solution weakly acidulated with sulphuric acid. In strong acid solution (1:5) it is soon decolorized, owing to its rapid hydrolysis into hydroperoxide. If a grain of manganous acetate be added to an excess of the solution, a red coloration is produced which is somewhat obscured by the formation of manganese dioxide. If dilute sulphuric acid be previously added, the solution assumes the characteristic color of permanganic acid, and no manganese dioxide is formed unless considerable of the manganous salt is added. In strong sulphuric acid solution (1:5) the formation of permanganic acid is prevented. If potassium permanganate be added drop by drop to a solution containing both acetperacid and hydroperoxide, weakly acidulated with sulphuric acid, it is quickly decolorized until the hydroperoxide is destroyed. At this point the manganous salt begins to be re-oxidized to permanganic acid, and the solution is soon deeply colored.

An attempt to estimate a known amount of hydroperoxide in the presence of a solution of acetic peroxide, which had stood for two hours, gave a result a little low, as might be expected, for, in the time required to make the titration, a small amount of the manganous salt formed by oxidation of hydroperoxide is reoxidized by the peracid to permanganic acid, thus decreasing the required amount of the latter.

The solution of acetperacid does not oxidize alcohol, which is shown by the fact that the amount of peracid in a solution to which alcohol had been added had not decreased on standing twenty-four hours. The same result was obtained by adding crotonic acid to a solution.

The solution gives no precipitate on addition of the acetates

of silver, lead, mercury, or copper. With silver oxide and lead monoxide a rapid evolution of oxygen occurs. A solution of basic lead acetate shows the same behavior. Manganese dioxide shows no catalytic action, but is oxidized to permanganic acid.

As the simplest representative of the organic peracids, it is quite probable that this substance will be found suitable for oxidizing purposes in certain cases, as has already been the case with the similarly constituted sulphuric peracid (Caro's reagent).¹ Its suitability for such purposes lies in the following facts: (1) It is easily prepared; (2) a very concentrated solution may be made by continued hydrolysis of an excess of the peroxide; (3) it is an organic oxidizing agent and the reduction-product is unobjectionable.

As has already been observed, the acetic peroxide when caused to explode does so with great violence. During the work with this substance an explosion was never experienced except when it was heated or subjected to unnecessary friction. To prepare the substance pure, it is not necessary to handle it as the crystallization may be brought about in a flask, the mother-liquor removed by decantation, and the crystals washed and dried in a vacuum without removing them from the flask. This method was employed repeatedly without accident. In cases where the presence of ether is unobjectionable, the solution of acetic peracid may be made by dissolving in water the concentrated ethereal solution of the crude product.

Propionic Peroxide.

Preparation.—The method employed in making acetic peroxide was used also in this case. Eight and a half grams of propionic anhydride were dissolved in 100 cc. of ether and cooled to 15°. Six grams of 95 per cent. barium peroxide were suspended in 40 cc. of water, cooled to 15°, and added to the ethereal solution. On shaking for fifteen minutes the barium peroxide was dissolved. The maximum amount of propionic peroxide was not present in the solution until a total of 7.5 grams of barium peroxide had been added. Until this point was reached the solution still contained unchanged anhydride (found by comparing the amount of N/10 potassium hydroxide required by 1 cc. of

¹ Ber. d. chem. Ges., 32, 1676, 3625.

solution with amount of N/10 thiosulphate required). At the point of maximum yield the anhydride had disappeared and the addition of more barium peroxide decreased the amount of propionic peroxide. The necessity for using an excess of barium peroxide is thus found, and that the yield of propionic peroxide (4 grams) does not equal the theoretical is also accounted for. The reaction, therefore, takes place according to the following equation:



The ethereal solution was dried over calcium chloride, the ether evaporated in a vacuum, and the last traces completely removed by means of a current of dry air at 35° in a vacuum. The resulting product was analyzed as follows: The active oxygen was estimated by dissolving in 80 per cent. acetic acid containing potassium iodide, and allowing to stand for one-half hour for complete liberation of the iodine. It was then diluted and the latter estimated by N/10 thiosulphate. A blank experiment was then made under the same conditions and the correction applied.

As a substitute for the difficult elementary analysis, the amount of potassium hydroxide required to convert a known amount into potassium propionate was determined. This method has already been spoken of under acetic peroxide. The substance was dissolved in an excess of N/10 potassium hydroxide, heated for ten minutes on a water-bath, and the excess of potassium hydroxide then determined by titration.

The residue of propionic peroxide, on removal of the ether, gave active oxygen and acid values both a little high. This could be accounted for only by assuming the presence of a small amount of acetic peroxide. This was confirmed by repeatedly shaking the product with small portions of water. The first washings contained much more active oxygen than the latter, the content of which soon became constant, representing the solubility of the pure propionic peroxide. Ten cc. required 10.9 cc. N/10 thiosulphate.

The saturated solution is therefore 0.109 normal and contains 15.9 grams per liter.

The washed product was again taken up with ether and dried.

On complete removal of the solvent it gave analytical results showing that it was pure propionic peroxide:

0.1595 gram required 21.7 cc. N/10 thiosulphate; calculated, 21.85 cc.

0.1395 gram required 19.0 cc. N/10 potassium hydroxide; calculated, 19.1 cc.

The presence of a more highly oxidized form was at first suspected in the crude product. This is made impossible by the fact that the potassium hydroxide and thiosulphate values, while both high, were exactly the same. The acetic peroxide was probably formed from acetic anhydride present as an impurity in the propionic anhydride employed.

The pure propionic peroxide is miscible with all the ordinary solvents. When heated to 80° a slow effervescence sets in, which continues until the decomposition is complete. Hydrocarbons and carbon dioxide are evolved, and the residue is a gum which dissolves completely in sodium carbonate and is again precipitated on acidifying. When subjected suddenly to a high temperature the peroxide explodes, but without the violence and detonation of acetic peroxide. At -20° it could not be induced to solidify. Owing to its instability, no attempt was made to distil it.

Hydrolysis.—In the case of acetic peroxide a rough idea of the course of its hydrolysis was obtained by determining the immediate liberation of iodine from time to time. In the case of propionic peroxide the progress of the reaction is shown quite nicely by this method. In dilute acetic acid the unhydrolyzed peroxide affects potassium iodide very slowly, so that by working quickly it is possible to estimate the amount of peracid in a solution accompanied by peroxide, without much error due to the latter.

The following table shows the behavior of a solution of propionic peroxide at a temperature of 20°. Five cc. of the solution required a total of 10.8 cc. N/20 thiosulphate. The numbers under "immediate iodine" represent the amount of thiosulphate required by 5 cc. of the solution from time to time. The relative values of the reaction-constant,

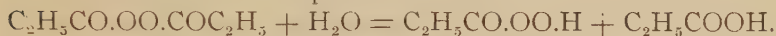
$$\left(K = \frac{1}{t} \log \frac{a}{a-x} \right),$$

have been calculated, assuming the reaction to be of the first

order. In the first three determinations there is a remarkably good agreement in this value, as an error of 0.1 cc. in the titration numbers is sufficient to account for the variation. The lowness of the fourth value is probably due to the formation of hydroperoxide in the more concentrated solution of peracid.

Time in hours.	Immediate iodine. cc.	Reaction-constant.
3.0	3.0	471
6.5	5.4	463
11.5	7.6	459
23.0	9.8	449

The reaction is to be expressed as follows:



After twenty-four hours hydroperoxide may be detected in the solution. In its chemical behavior propionic peracid is not to be distinguished from acetic peracid.

Crotonic Peroxide.

Crotonic Anhydride.—The general method proposed by Autenrieth¹ was employed with very satisfactory results. One hundred grams crotonic acid were boiled with 350 grams acetic anhydride for twenty-four hours, with reflux condenser. The acetic acid and excess of anhydride were then distilled off under diminished pressure. The residue was taken up with ether and shaken out with the requisite amount of sodium carbonate for removal of unchanged acid. It was then dried over calcium chloride and, after distilling off the solvent, was fractionated under diminished pressure. About 60 grams of practically pure anhydride, boiling within 4° to 5°, were finally obtained. The amount of mixed anhydride formed was very small. The highly purified crotonic anhydride boils at 128° to 130°, under 19 mm., with slight decomposition. Its specific gravity at 29°, compared with water at the same temperature, is 1.0338. It does not solidify at —15°.

Analysis: 0.1734 gram substance gave 0.3956 gram CO₂ and 0.1019 gram H₂O.

	Calculated for C ₈ H ₁₀ O ₃ .	Found.
C	62.34	62.21
H	6.49	6.53

¹ Ber. d. chem. Ges., 34, 168.

0.1000 gram required 26.0 cc. N/20 potassium hydroxide to neutralize; calculated, 26 cc.

Preparation of Peroxide.—Seven and eight-tenths grams anhydride were dissolved in 100 cc. ligroin and added to 3.4 grams of hydroperoxide in 8 per cent. solution. This mixture was cooled to 15° , and a saturated solution of barium hydroxide added in portions of 10 cc., shaking after each addition until the barium dioxide had disappeared. The mixture was kept cooled to 15° , and the course of the reaction was followed by estimation of the active oxygen content of 1 cc. of the solution from time to time. The latter showed a maximum value after the addition of 100 cc. (3.14 grams) of barium hydroxide. There was present in the solution at this point active oxygen to account for 3.9 grams of crotonic peroxide. On removing the ligroin solution and partially evaporating the solvent, the peroxide separates as crystals on cooling. Only about 2 grams of these crystals were obtained, the remaining product separating as an oil. This oil is probably an oxidation-product of the unsaturated crotonic anhydride in alkaline solution, for it has been observed that hydroperoxide and peracids are much more powerful oxidizers in the presence of alkalis than in neutral or acid solution. The crystals which separated from the ligroin solution were practically pure. The pure substance consists of needles and irregularly shaped plates, and melts at 41° . It is odorless and explodes gently on heating. It does not decompose on long standing. It is soluble in all of the ordinary solvents.

The active oxygen was determined by dissolving in 10 per cent. acetic acid and adding a solution of potassium iodide acidulated with dilute sulphuric acid. A blank experiment was made and the correction applied.

0.1182 gram substance required 13.8 cc. N/10 thiosulphate; calculated 13.9 cc.

0.1249 gram treated with excess of N/10 potassium hydroxide required 30.7 cc. to neutralize: calculated 29.4 cc.

This method of analysis is evidently not applicable in the case of an unsaturated peroxide. The elementary analysis was therefore made.

0.1328 gram substance gave 0.2737 gram CO_2 and 0.0705 gram H_2O .

	Calculated for $C_8H_{10}O_4$.	Found.
C	56.47	56.20
H	5.88	5.81

Hydrolysis.—This substance was selected on account of its being crystalline, with the intention of isolating the peracid formed. The slowness with which it hydrolyzes, however, renders it unsuitable for such study.

An excess of peroxide was added to water contained in a glass-stoppered flask and shaken at 25° for several days. The progress of the hydrolysis was ascertained by removing 25 cc. of the solution at intervals and determining the immediate liberation of iodine. The difference between immediate iodine and total iodine is seen to be the same in each case, representing the solubility of the unchanged peroxide, which remains constant. There is also seen to be a regular increase in the amount of peracid. The latter, therefore, appears to have no oxidizing action on the unsaturated carbon atoms.

Time in days.	Immediate iodine. Cc. in N/10 thiosulphate.	Total iodine. Cc. N/10 thiosulphate
2	1.35	4.1
4	2.7	5.5
8	5.2	7.9

A portion of the solution removed, after standing for one month, had lost only one-fourth of its active oxygen, which was then present almost entirely as peracid. At this time hydroperoxide could just be detected by means of the chromic acid test.

Another completely hydrolyzed solution of 0.3 gram peroxide in 50 cc. water was extracted with ligroin, thereby removing only a trace of peracid. On extracting twice with ether the peracid was completely removed, together with crotonic acid. On evaporating the ether a crystalline residue remained, which possessed the characteristic peracid odor.

Benzoic Acetic Peroxide.

The substance dissolved in dilute acetic acid liberates the theoretical amount of iodine from potassium iodide. Its solubility in water at 25° amounts to 0.639 gram per liter.¹ This

¹ Freer and Novy: *Loc. cit.*

solution, on standing, suffers not only a change to peracid, as noted by change in the amount of iodine liberated immediately, but soon becomes turbid, owing to the separation of the insoluble benzoic peroxide. By adding an excess of the peroxide to water and shaking the mixture to keep the solution saturated, the benzoic peroxide gradually accumulates, while the soluble products remain in the solution. In this way a more concentrated solution of the latter is obtained, suitable for study.

Four grams of the peroxide were added to 250 cc. water and shaken at 25°. At intervals, given in the table below, a portion of the solution was filtered through glass wool, 10 cc. of the filtered solution removed, and its immediate and total liberation of iodine estimated with N/10 thiosulphate. After forty-two hours the presence of hydroperoxide was plainly shown by the chromic acid test. This accounts for the gradual increase in the amount of "additional iodine," which is made up of unchanged peroxide and hydroperoxide. The numbers in the column under "immediate iodine" give a general idea of the rate of formation of peracid. As this experiment was continued through a considerable space of time and peracids in solution are unstable, they represent less than the total amount of peracid formed.

The rate of hydrolysis, as represented by the rate at which the solution takes on active oxygen, is found to increase slowly during the course of the experiment, probably owing to the increased solubility of the peroxide and to the catalytic action of the acid formed.

Time in hours.	Immediate iodine.	Additional iodine.
21	3.8	0.8
42	8.0	0.9
52.5	10.3	1.0
73.5	14.3	1.3

The following experiments were performed with accurately weighed amounts of pure peroxide:

(1) 0.5180 gram was added to 50 cc. water and shaken in a sealed flask at 25° until the change was complete. As previously mentioned, a solution of benzoic acetic peroxide becomes decidedly turbid on standing, and this fact made it possible to ascertain

the completeness of the reaction. After four days the flask was opened, the residue carefully filtered and washed, the washings being added to the filtrate. The residue consisted of 0.1726 gram pure benzoic peroxide (m. p. $107^{\circ}.5$). As the filtration was made through glass wool the benzoic peroxide was most conveniently determined by estimating the active oxygen. Experiments with pure benzoic peroxide showed the following method to be accurate: The peroxide is dissolved in 80 per cent. acetic acid containing potassium iodide and allowed to stand one hour, when the solution is diluted and the iodine estimated. A correction, determined by a blank experiment under the same conditions, is then applied. The filtrate was found to require 39.5 cc. N/10 thiosulphate for "immediate" iodine and 2.5 cc. for "additional." The total active oxygen obtained from the products of hydrolysis amounted to 0.0028 gram-molecule of the original peroxide, while 0.00288 gram-molecule had been taken. The loss is due to the instability of the solution of peracid. The per cent. of active oxygen which separated as benzoic peroxide was 24.7.

(2) 0.5100 gram was added to 100 cc. water and the previous experiment repeated. It was removed in thirty hours. 0.1416 gram benzoic peroxide was formed. The solution required 43.8 cc. N/10 thiosulphate. The total active oxygen recovered amounted to 0.00277 gram-molecule, while 0.00283 gram-molecule had been used. The per cent. represented by benzoic peroxide was 20.6.

(3) 0.6211 gram was shaken with 250 cc. water, twenty-four hours being necessary to complete the change. 0.1510 gram benzoic peroxide was formed. The solution required 54.8 cc. N/10 thiosulphate. A total of 0.00336 gram-molecule was recovered while 0.00345 had been used. 18.1 per cent. of the active oxygen separated as benzoic peroxide.

It will be noted that the amount of benzoic peroxide formed is decreased by using more water. From this it may be inferred that the rate of formation of this substance increases as the process progresses.

Further Examination of the Solution.—From previous work we might expect the solution to contain either benzoic peracid or acetic peracid, or both, together with hydroperoxide.

0.6035 gram of pure peroxide was shaken with 50 cc. water at 25° for two and one-half days, the change being complete in this time. The solution was then filtered from the benzoic peroxide, cooled to 15°, and 2 grams acetic anhydride added and dissolved by shaking. The solution was kept cooled to 15° and soon became turbid, owing to the separation of an oil. On scratching the side of the vessel with a glass rod, the oil solidified and separated at the bottom as crystals. After standing for one-half hour the supernatant liquid became perfectly clear, and the addition of more acetic anhydride produced no further separation. The crystalline product was separated from the solution and was found to consist of pure benzoic acetic peroxide. The crude substance melted at 37° to 38°; recrystallized at 38° to 39°. 0.1496 gram required 16.6 cc. N/10 thiosulphate; calculated 16.6 cc. A solution of benzoic peracid, treated with acetic anhydride under the same conditions, showed the same formation of benzoic acetic peroxide. The formation of the latter in the hydrolyzed solution is, therefore, accounted for by the presence of benzoic peracid.

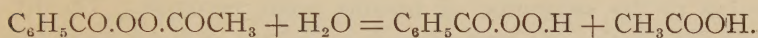


The filtrate from the crystalline peroxide was allowed to stand an hour for the hydrolysis of unchanged acetic anhydride, and was then extracted three times with one-third volume of pure ether in order to remove all benzoic acetic peroxide or benzoic acid, and any unchanged benzoic peracid. The ethereal solution was then treated with sodium carbonate solution which was added until, after shaking thoroughly, it remained permanently alkaline.

The ethereal solution, on evaporation, left a small amount of residue having the very penetrating odor of acetic peroxide. This would indicate the presence of acetic peracid in the original solution, were it not true that this solution contained a small amount of hydroperoxide. The alkaline extract was acidified and extracted thoroughly with ether. On evaporation there remained a residue of less than 0.02 gram of benzoic acid. A blank experiment, in which 0.1 gram of benzoic acid was subjected to

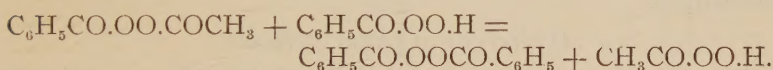
exactly the same treatment, resulted in its complete recovery. A solution of benzoic peracid, on standing, slowly changes to benzoic acid. As the above solution had stood two and one-half days and contained considerable benzoic peracid, the presence of the small amount of benzoic acid obtained is easily accounted for, and it may be concluded that the primary hydrolysis of the peroxide results in the formation of no benzoic acid. This experiment also illustrates the ease with which a peracid in aqueous solution may be acetylated, and so completely removed from the acid accompanying it.

Benzoic acetic peroxide, therefore, hydrolyzes according to the following equation:



The possible hydrolysis into acetic peracid and benzoic acid is excluded, or extremely minimized by the absence of benzoic acid.

From the three quantitative experiments previously detailed, it can be seen, however, that the total amount of peracid in solution is much in excess of the possible amount of benzoic peracid, taking into consideration the amount of benzoic peroxide which has been formed. From this it might be concluded that the solution contains acetic peracid. The presence of the latter may be explained by the following reaction:



This would also explain the formation of benzoic peroxide. The formation of the latter might also be explained by the action of benzoic peracid on benzoic acid, and this explanation is suggested by the absence of benzoic acid. It was found, however, that benzoic peracid and benzoic acid remain together in solution indefinitely without the formation of a trace of peroxide, which would be recognized by its precipitation.

The following facts leave no doubt as to the accuracy of the explanation given. As already noted, a solution of benzoic acetic peroxide becomes turbid on standing. If a few drops of dilute sulphuric acid be added to the solution this turbidity is prevented. If, besides the acid, a solution of benzoic peracid be

added, the turbidity appears under exactly the same conditions where, without the peracid, it is prevented. This fact shows that the latter is a factor in the formation of the benzoic peroxide. Furthermore, from the analogy between peroxides and anhydrides which this work has brought out, and from the reactivity of peracids and anhydrides, it might be expected that the former would also react with peroxides. The fact, already noted, that the amount of benzoic peroxide formed increases with the use of less water, is to be attributed to the increased concentration of the benzoic peracid.

If a freshly prepared solution of acetic peroxide be treated with a solution of benzoic peracid, the solution quickly becomes turbid, owing to the separation of benzoic acetic peroxide. The hydrolyzed solution of acetic peroxide, of course, does not show this behavior.

A drop or so of acetic acid has the same effect in preventing, or at least retarding, the formation of benzoic peroxide. If benzoic acetic peroxide be hydrolyzed in 5 per cent. acetic acid, the formation of benzoic peroxide is altogether prevented. Such a solution, after standing three weeks, was evaporated in vacuum. The residue had a penetrating peracid odor and dissolved completely in sodium carbonate. There was, therefore, no benzoic peroxide formed, and none of the original peroxide remained unchanged.

Hydrolysis of Other Peracids.

The behavior of aqueous solutions of benzoic peracid and phthalic monoperacid was also investigated.

Benzoic peracid was prepared by Baeyer by the action of sodium ethylate on benzoic peroxide. As the substance can be preserved only a short time, it is best prepared in small quantities for experimental purposes in the following way: 24 grams of benzoic anhydride were pulverized and added to a solution of 11 grams potassium hydroxide in 250 cc. of 2.6 per cent. hydrogen peroxide, cooled to 0°. After shaking for five minutes, the anhydride had gone into solution and a considerable amount of flocculent benzoic peroxide had been formed. This was removed by filtering through glass wool. The filtrate was then acidified with cold, dilute sulphuric acid and extracted twice with a small

quantity of chloroform. On evaporating the solvent a residue of 11 grams remained, of which 2.8 grams were benzoic peracid.

The solution, in accord with previous experience, was found to change slowly to hydroperoxide and benzoic acid. The change was followed by comparing the immediate liberation of iodine in dilute acetic acid solution with the total liberation. The change was found to take place much more rapidly in a dilute sulphuric acid solution (1 per cent.), which indicates the hydrolytic nature of the process. The solutions were allowed to stand at room temperature. The numbers given in the tables represent cubic centimeters of N/10 thiosulphate required by 10 cc. of the solution.

The solution in sulphuric acid was treated with sufficient sodium acetate to neutralize it before estimating the "immediate" iodine.

Time in days.	Immediate.	Total.
0	9.6	9.6
10	8.2	8.7
20	7.2	8.0
30	5.9	6.9

Acidulated Solution.

0	9.6	9.6
10	4.9	8.7
20	3.1	8.4
30	1.6	8.1

Both solutions are ultimately changed completely into hydroperoxide, as indicated by the action on potassium iodide and the complete loss of odor. Furthermore, on saturating a 10 per cent. solution of hydroperoxide with benzoic acid it is impossible to detect the formation of any peracid.

The phthalic monoperacid of Baeyer was found to undergo the same change with much greater rapidity. When in solution one-half of this substance (N/2 in active oxygen) was found to be changed in twenty-four hours. At the end of four days the change was complete.

